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(54) **Clay composition and method of casting.**

(57) In a method of preparing a treated clay product, clay is heated such that kaolinite in the clay is converted to metakaolin, substantially no mullite being formed. The treated product may be combined with raw ball clay and/or china clay to provide compositions suitable for use in manufacturing china articles. The casting compositions enable the casting step to be accelerated and are particularly suitable for use in pressurised casting methods.

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Clay Composition and Method Casting

The present invention relates to materials for use in the manufacture of ceramic articles. In particular, the invention provides a composition that is suitable for use in the manufacture of china articles, for example vitreous china ware such as sanitary ware, and a method of making a china article in which the said composition is used.

In one known method of making china articles (the slip-casting method) an aqueous slip is introduced into a plaster mould. De-watering of the slip occurs through the plaster mould. After de-watering sufficient to form a cast article of the desired thickness has occurred, excess slip is drained from the mould, the article is allowed to harden and, after removal from the mould, is trimmed, dried, glazed and fired. In this method the de-watering step may take from 1 to 1½ hours and, typically, a further period of 1½ hours is required for hardening before the cast article can be removed from the mould.

In another known method (the pressurised casting method) an aqueous slip is placed in a mould and the mould is pressurised to accelerate de-watering of the slip. The mould may be of, for example, porous plastics material, mineral fibres, or sand/resin blocks. In one version of the pressurised casting method the mould is of porous plastics material and, at a pressure of 300 lb in^{-2} (2.1 X 10^6 Nm^{-2}), adequate de-watering may be accomplished within a period of from 8 to 10 minutes. In this version of the pressurised casting method, the following steps are generally carried out: the mould is filled with the slip, the mould is pressurised for a period of from 8 to 10 minutes, excess slip is drained from the mould, the article is consolidated by applying air pressure such that further de-watering of the material occurs through the mould, and the resulting cast article is then released and removed from the opened mould. The total time required for completion of these steps will normally be of the order of 12 to 15 minutes.

In the known methods discussed above an aqueous slip comprising china clay, ball clay, a flux and a filler is generally used. A typical aqueous slip might consist, for example, of 25% by weight china clay, 25% by weight ball clay, 20% by weight flux, 30% by weight filler and water in an amount which is sufficient to give a liquid slip of relatively low viscosity. Other ingredients, for example, a deflocculating agent, may be included. The flux may be, for example, a feldspar-containing flux, for example nepheline syenite, or any other suitable material which melts at the temperature to be used for the firing step to fuse the other ingredients together. The filler is normally a silica filler and may be for example sand, quartz or flint. Flint which has been fired at a temperature of the order of 1000°C and crushed may be used as the filler. The slip may comprise, in replacement of a part of the china clay and/or a part of the ball clay, from 5 to 15% grog (that is, ground faulty china ware). The grog is thus material which has already been subjected to conditions suitable for firing china, for example firing at a temperature of 1200°C. The thickness of the cast articles is normally in the region of from 8 to 10 mm.

The present invention provides a composition comprising

a treated clay product which has been prepared by heating clay, the heating conditions being such that kaolinite in the clay is converted to metakaolin, while substantially avoiding the formation of mullite; and

raw ball clay and/or raw china clay.

The term "raw" is used herein in relation to clay to mean a clay which has not been subjected, subsequent to its extraction from the ground, to conditions which would be likely to effect a crystalline transformation of any of the ingredients of the clay.

Preferably, the treated clay product has been prepared by heating ball clay. Advantageously, the composition comprises the treated ball clay and raw ball clay in a ratio of from 1:2 to 4:1 by weight. Instead of, or in addition to, the raw ball clay, the composition may comprise raw china clay, the treated ball clay product and the china clay being present in a ratio of from 1:1 to 7:4 by weight.

The treated ball clay product may be obtained for example, by heating ball clay to a temperature of from 560°C to 1130°C for a time of from 10 minutes to 2.5 hours. The temperatures in the upper part of the specified temperature range correspond to the shorter heating times and the temperatures in the lower part of the specified temperature range correspond to the longer heating times.

Preferably, the treated ball clay product has been obtained by heating ball clay until the bulk density of the clay is reduced to within the range of from 1.75 to 2.0 g/cm^3. The bulk density of the ball clay may be monitored during heating, the clay being heated until the bulk density of the clay is reduced to within a desired range. By selecting an appropriate desired range it is possible to ensure that the treated product will have particularly good properties.

Preferably the heating conditions in preparation of the treated clay product are such that substantially all the kaolinite in the clay is converted to metakaolin.

The possible range of temperatures and the length of time, required at a chosen temperature within that range, to convert kaolinite, and advantageously substantially all the kaolinite, in ball clay to metakaolin with substantially no conversion of the metakaolin to mullite, may depend on the ball clay used. The term "ball clay" as used herein encompasses any plastic clay and, in particular, is not limited in terms of the geographical location of the source of the clay. Thus, one type of ball clay (having a chemical analysis of SiO_2 (56.2%), TiO_2 (1.2%), Al_2O_3 (28.6%), Fe_2O_3 (1.0%), CaO (0.2%), MgO (0.3%), K_2O(1.8%) and Na_2O (0.2%), loss on ignition of 10.6% and a calculated mineralogy (Mica Convention) of 55% kaolinite, 15% potash mica, 2% soda mica, 22% quartz and 2% carbonaceous matter) may be heated in accordance with the invention to a temperature within the range of from 570° C to 1130° C. (The percentages given above and elsewhere herein are by weight.) At a temperature of 1130° C, a heating time in the region of 10 minutes is sufficient to convert kaolinite in the ball clay to metakaolin, substantially no mullite being formed; the bulk density of the product so obtained is in the order of 2 g/cm^3. If, however, a lower temperature is used a longer heating time will be required. For example, at a temperature of 570° C a heating time of more than two hours may be required.

Another type of ball clay (having a chemical analysis of SiO_2 (53.4%), TiO_2 (1.2%), Al_2O_3 (29.8%), Fe_2O_3 (1.0%) CaO (0.2%), MgO (0.3%), K_2O (2.1%), Na_2O (0.3%), loss on ignition of 11.7% and a calculated mineralogy (Mica Convention) of 53% Kaolinite 17% potash Mica, 4% soda Mica, 20% quartz and 3% carbonaceous matter) may be heated in accordance with the invention to a temperature within the range of from 560° to 1080° C. At a temperature of 1080° C a heating time of in the region of 10 minutes will be sufficient whereas at a temperature of 560° C a heating time of more than two hours may be required. Determination of appropriate time/temperature regimes for other ball clays is a matter of routine experiment. The heating may be carried out in the presence of air.

While in the most preferred form of the invention the treated clay product is a product which has been prepared by heating ball clay, it can also be a treated product prepared by heating china clay, appropriate time/temperature regimes for effecting transformation of kaolinite to metakaolin while substantially avoiding the formation of mullite then being determinable by routine experiment. Mixtures of ball clay and china clay can also be used.

The composition of the invention is suitable for use in the manufacture of china articles, especially vitreous china articles, for example sanitary ware. The use of the composition of the invention as a component of a casting composition for the manufacture of china enables the casting step to be accomplished more quickly than in processes in which the previously known casting compositions are used.

When the composition is to be used in the manufacture of china, the treated clay product to be mixed with the raw ball clay and/or raw china clay is preferably ground. The treated clay product may be ground in a ball mill to the desired degree of fineness. Preferably, the treated clay product is ground such that at least 90% by weight of the ground product has a particle size of less than 20μ. Particles of size greater than 20μ may be removed by screening and, if desired, recycled to the grinding step.

The composition may be prepared by mixing the treated clay product with raw ball clay and/or raw china clay, the mixture so obtained being shaped, dried and divided. For example, the composition including the treated clay product and the raw ball clay and/or the raw china clay may be extruded as elongate rods which may then be dried and divided into pellets. The composition is advantageously dried to a moisture content of not less than 7%, wet basis. The dried composition is in general brittle and may disintegrate into pellets without assistance. The composition may then be combined with a flux and a filler and, if desired, with further ball clay and/or china clay, for use in the manufacture of china articles, for example by the slip-casting or pressurised casting methods.

The present invention further provides a casting composition for use in the manufacture of china articles, the composition comprising:

a treated clay product which has been prepared by heating clay, the heating conditions being such that kaolinite in the clay is converted to metakaolin, while substantially avoiding the formation of mullite;
raw ball clay;
raw china clay;
a suitable flux; and,
a suitable filler.

Preferably, the treated clay product has been prepared by heating ball clay. The casting composition preferably comprises from 10 to 20 parts by weight of the treated ball clay product, from 5 to 20 parts by weight of raw ball clay, and from 10 to 35 parts by weight china clay, the combined weight of the flux and filler being not less than the combined weight of the treated ball clay product, the raw ball clay and the china clay.

While the use of a treated clay product prepared by heating ball clay is especially preferred in the casting composition of the invention, the treated clay product can also be a product which has been prepared by heating china clay.

For use in the manufacture of china, the casting composition may further comprise water. The amount of water is preferably such that the composition is flowable. For example, the composition may further comprise from 10 to 30 parts by weight water in addition to the water present in the other constituents. The casting composition may advantageously comprise an effective amount of a deflocculant and may comprise other ingredients, for example dispersants and colouring agents. The flux may be, for example, a feldspar-containing flux. The filler may be, for example, a filler selected from quartz, sand and flint.

In addition, the present invention provides a method of manufacturing a china article, comprising placing in a mould an aqueous slurry comprising a treated clay product which has been prepared by heating clay, the heating conditions being such that kaolinite in the clay is converted to metakaolin, while substantially avoiding the formation of mullite, the slurry further comprising raw ball clay and/or raw china clay, removing at least some water from the slurry, draining from the mould any remaining slurry, removing the article from the mould, drying and firing the article. The aqueous slurry preferably further comprises raw ball clay, china clay, a flux and a filler. In a preferred method, the aqueous slurry comprises from 10 to 20 parts by weight of the treated ball clay product, from 5 to 20 parts by weight of raw ball clay, from 10 to 35 parts by weight china clay, the combined weight of the flux and filler being not less than the combined weight of the treated ball clay product, the raw ball clay and the china clay.

The treated product may be a treated product which has been prepared by heating china clay.

The method of the invention permits casting to be accomplished in a reduced time as compared with the previously known methods. Preferably, the mould is pressurised during the removal of water from the slurry. For example, a pressure of greater than 40lb in^{-2} (2.7 X 10^{5}Nm^{-2}), more especially a pressure of from 40 to 700lb in^{-2} (2.7 X 10^{5} to 4.8 X 10^{6}Nm^{-2} , may be maintained in the mould. Using the method of the invention it is possible to accomplish a de-watering step in the pressurised casting method, using a pressure of 300lb in^{-2} (2.1 X 10^{6}Nm^{-2}), in a period of from 2 to 4 minutes. An article may thus be cast in the pressurised casting method in a total time of from 4 to 8 minutes, from filling the mould to removal of the cast article from the mould.

When a pressurised casting mould is used, the casting composition of the invention, including water, may be heated to 40°C before introduction into the mould. Preferably, the casting composition is agitated continuously immediately prior to the transfer to the mould to maintain an even distribution of the components of the casting composition. On removal from the mould the cast article may be dried, finished (trimmed), and fired by any suitable method, for example by methods used in previously known casting processes. If desired, the cast article may be trimmed before drying. On removal from the mould the cast article may have a moisture content of, for example 20% wet basis. The article may be dried in open air at ambient temperature. Advantageously, however, the article is force-dried, for example microwave-dried, to reduce the moisture content by from 1 to 5%, especially from 1 to 2%, wet basis and is subsequently further dried in open air at ambient temperature.

The casting composition of the invention is particularly suitable for use in the manufacture of vitreous china. The article may be glazed by any suitable method.

A further advantage of the casting composition of the invention is that the cast article is suitable for quick firing. Firing may be carried out by subjecting the articles manufactured according to the invention to a temperature which increases continuously or stepwise to a maximum temperature of the order of 1200°C, which may be maintained for a period of up to 5 hours, the temperature then being reduced gradually in continuous or stepwise manner. When the article is quick-fired a total time of 10 hours is required for the firing step.

The casting composition of the invention may be used in the manufacture of sanitary ware, for example, soap dishes, wash basins and other vitreous china products, for example airline trays.

The following Examples illustrate the invention:

Example 1(a)

A quantity of shredded ball clay having the following composition: SiO_2 (67.5%), TiO_2 (1.5%), Al_2O_3 - (21.7%), Fe_2O_3 (0.8%), CaO (0.18%), MgO (0.28%), K_2O(2.37%) Na_2O (0.26%), loss on ignition of (5.8%) and having a calculated minerology (Mica Convention) of 32% Kaolinite, 20% Potash Mica, 3% Soda Mica, 42% Quartz and 0.25% carbonaceous matter
is heated to 1000°C for a period of ten minutes in a Brisesco belt kiln, giving a product bulk density of 1.80 g/cm^3. The material is allowed to cool naturally to ambient temperature and is then ground in a hammer mill and classified in a British Rema Classifier, particles of greater than 40μ being removed. The ground product

has a particle size distribution of:-

size:	20μ	10μ	5μ	2μ	1μ
% less than	92	77	59	40	25
(as determined using a Micromeritics Sedigraph).					

Example 1(b)

The product from Example 1(a) is included as a component in a method for manufacturing a sanitary ware body, in which method

16% by weight ground treated ball clay product prepared as described in Example 1(a);
8% by weight raw ball clay;
26% by weight china clay;
30% by weight quartz; and
20% by weight nepheline syenite

are mixed with water to a slip fluid density of 1.825 gcm^{-3}. 0.28% by weight (based on the total weight the mixture, excluding water) of a mixture of sodium silicate grade C100 and anhydrous sodium carbonate at a ratio of 3:1 being added as a deflocculant.

This slip was heated to 40° C and pressure cast at 20 bar. The material produces a cast thickness of 9 millimetres in under four minutes pressing time. The cast body is then processed as in previously known methods to give a vitreous china body.

Example 2(a)

A quantity of shredded ball clay having the composition given in Example 1(a) is rotary calciner fired to a temperature of 800° C for 2 hours giving a product bulk density 1.85g/cc.

This material is wet ball milled for 2 hours to give a suspension of 50% solids. The product has a particle size distribution of:-

size:	20μ	10μ	5μ	2μ	1μ
%less than:	97	84	62	45	36
(as determined using a Micromeritics Sedigraph).					

Example 2(b)

The product of Example 2(a) is included as a component in a method for manufacturing a sanitary ware body, in which method

13.2% by weight ground treated ball clay product prepared as described in Example 2(a) above;
10.8% by weight raw ball clay;
26% by weight china clay;
30% by weight quartz; and
20% by weight nepheline syenite

are mixed with water to a slip fluid density of 1.825 gcm^{-3}. 0.28% by weight (based on the total weight of the mixture excluding water) of a mixture of sodium silicate grade C100 and anhydrous sodium carbonate at a ratio of 3:1 being added as a deflocculant.

This slip was heated to 40° C and pressure cast at 20 bar. The material produces a cast thickness of 9 millimetres in unde[illegible]our minutes pressing time. The cast body [illegible]en processed as in previously known methods to give a vitreous china body.

Claims

1. A composition comprising
a treated clay product which has been prepared by heating clay, the heating conditions being such that kaolinite in the clay is converted to metakaolin, while substantially avoiding the formation of mullite; and
raw ball clay and/or raw china clay.

2. A composition as claimed in claim 1, wherein the treated clay product has been prepared by heating ball clay.

3. A composition as claimed in claim 2 which comprises the treated ball clay product and raw ball clay in a ratio of from 1:2 to 4:1 by weight.

4. A composition as claimed in claim 2 or claim 3 which comprises the treated ball clay product and raw china clay in a ratio of from 1:1 to 7:4 by weight.

5. A composition as claimed in any one of claims 2 to 4, wherein the treated ball clay product has been obtained by heating ball clay to a temperature of from 560°C to 1130°C for a time of from 10 minutes to 2.5 hours.

6. A composition as claimed in any one of claims 2 to 5, wherein the treated ball clay product has been obtained by heating ball clay until the bulk density of the clay is reduced to within the range of 1.75 to 2.0g/cm^3.

7. A composition as claimed in claim 1, wherein the treated clay product has been prepared by heating china clay.

8. A composition as claimed in any one of claims 1 to 7, wherein at least 90% by weight of the treated clay product has a particle size of less than 20μ.

9. A composition as claimed in any one of claims 1 to 8, which is in pellet form.

10. A method of preparing a composition according to any of claims 1 to 9, wherein the treated clay product is mixed with raw ball clay and/or raw china clay, the mixture so obtained being shaped, dried and divided.

11. A casting composition for use in the manufacture of china articles, the casting composition comprising a composition according to any of claim 1 to 8.

12. A casting composition for use in the manufacture of china articles, the composition comprising
a treated clay product which has been prepared by heating clay, the heating conditions being such that kaolinite in the clay is converted to metakaolin, while substantially avoiding the formation of mullite;
raw ball clay;
raw china clay;
a suitable flux; and
a suitable filler.

13. A casting composition as claimed in claim 12, wherein the treated clay product has been prepared by heating ball clay.

14. A casting composition as claimed in claim 13, which comprises from 10 to 20 parts by weight of the treated ball clay product, from 5 to 20 parts by weight of raw ball clay, from 10 to 35 parts by weight of china clay, the total combined weight of the flux and filler being not less than the combined weight of the treated ball clay product, the raw ball clay and the china clay.

15. A casting composition as claimed in claim 12, wherein the treated clay product has been prepared by heating china clay.

16. A casting composition as claimed in any of claims 13 to 15, wherein the composition further comprises water.

17. A method of manufacturing a china article, comprising placing in a mould an aqueous slurry comprising a treated clay product which has been prepared by heating clay, the heating conditions being such that kaolinite in the clay is converted to metakaolin, substantially avoiding the formation of mullite, the slurry further comprising raw ball clay and/or raw china clay, removing at least some water from the slurry, draining from the mould any remaining slurry, removing the article from the mould, drying and firing the article.

18. A method as claimed in claim 17, wherein the aqueous slurry further comprises raw ball clay, china clay, a flux and a filler.

19. A method as claimed in claim 17 or claim 18, wherein the treated clay product has been prepared

by heating ball clay.

20. A method as claimed in claim 19, wherein the aqueous slurry comprises from 10 to 20 parts by weight of treated ball clay product, from 5 to 20 parts by weight of raw ball clay and from 10 to 35 parts by weight of china clay, the combined weight of the flux and filler being not less than the combined weight of the treated ball clay product, the ball clay and the china clay.

21. A method as claimed in claim 17 or claim 18, wherein the treated clay product has been prepared by heating china clay.

22. A method as claimed in any one of claims 17 to 21, wherein a pressure of not less than 40lb in^{-2} (2.7 X $10^5 Nm^{-2}$ is maintained in the mould.

23. The use of a composition comprising a treated clay product which has been prepared by heating clay, the heating conditions being such that kaolinite in the clay is converted to metakaolin, while substantially avoiding the formation of mullite, the composition further comprising raw ball clay and/or china clay, in the manufacture of vitreous china articles.

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EUROPEAN SEARCH REPORT

Application Number

EP 89 30 9482

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GB-A-1 317 735 (HUBER CORP.) * Claims 1-10; page 6, lines 26-38 * ---	1-23	C 04 B 33/04 C 04 B 33/24
A	DE-A-2 140 982 (KOMBINAT VEB KERAMISCHE WERKE HERMSDORF) * Claims 1-4; page 4, paragraph 2 * -----	1-23	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 04 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06-11-1989	LUETHE H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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